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Cooperative Structure Direction in the Synthesis of Microporous Materials: Preparation and Crystal Structure of TREN-GaPO

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Following the discovery of the microporous aluminophosphates by Wilson et al.,[1] the number of new classes of metal phosphate molecular sieves has rapidly increased. The addition of fluoride to the synthesis by Guth et al.[2] aids in the crystallization of many of these metal phosphates, in particular gallium, and allows for crystal growth in neutral or acidic media. In many of these cases the fluoride is incorporated into the structure. In cloverite,[3] GaPO-LTA,[4] and ULM-5,[5] for example, fluoride is found in the centers of the double 4-rings of these structures, suggesting that it stabilizes this unique feature of these frameworks. Besides existing as an extraframework species, fluoride is also found in the coordination sphere of gallium.[6] It is believed that in this instance it aids in the stabilization of the high coordination environment of the gallium and adds rigidity to the structure through Ga−F−Ga bonds. By allowing the gallium to take on 4-, 5-, or 6-fold coordination, the synthesis of a wide variety of new, complex architectures, different from the zeolites and $AlPO_4$'s, is possible.

Nonaqueous approaches, i.e., replacing water with an alcohol or glycol, have allowed access to compositions that are not possible through conventional aqueous routes. Kuperman et al. used pyridine as the solvent, together with HF and another amine, to synthesize single crystals of siliceous ferrierite and some aluminophosphates.[7] The unique cooperativity between propylamine and pyridine in the growth of ferrierite[8] suggested to us that "synergistic templating" might be possible in other systems as well. Ongoing research on solution templating in microporous and mesoporous[9] materials led us to study the competitive formation of microporous materials using two amines. Do the amines work cooperatively or separately? If the amines do work in parallel, this has implications for the ability to control the pore structure through the shrewd choice of amines. By combining the use of fluoride and two amines, tris(2-aminoethyl)amine (TREN) and pyridine, we have synthesized a new, open-framework gallium oxyfluorophosphate, TREN−GaPO.

The synthesis of TREN−GaPO was carried out hydrothermally in a 23 mL Teflon-lined Parr acid digestion bomb using the following molar gel composition: 0.88 TREN:Ga_2O_3:1.3 P_2O_5:32.1 pyridine:5.2 HF:86 H_2O. Gallium sulfate [Alfa] was first dissolved in water. To the gallium sulfate solution , H_3PO_4 [85 wt %, Fisher], HF/pyr [70 wt % HF, Aldrich (HF solution and pyridine, in the appropriate molar ratios, works just as well)], and

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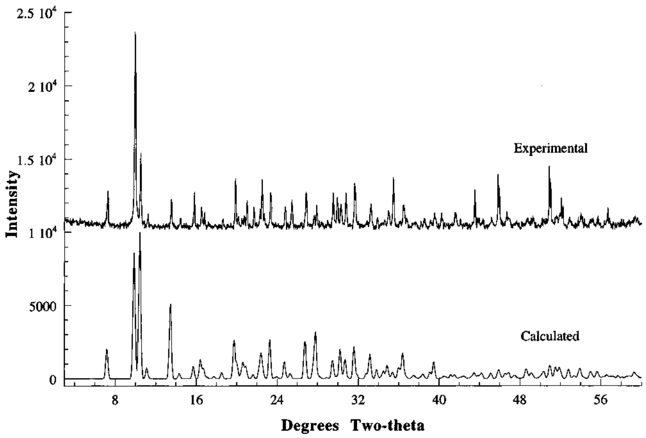

Figure 1. (a, top) Observed powder X-ray diffraction pattern of a TREN−GaPO preparation; the pattern contains additional peaks due to the presence of other phases (see text). (b, bottom) Simulated powder X-ray diffraction patterns of TREN−GaPO.

pyridine [Fisher, PYR] were added respectively and stirred for 10 min. TREN [Aldrich] was then added and the resulting clear solution (pH ~ 5) was stirred for 2 h before placing the reaction into a force-draft oven at 170 °C for 4 days. At the completion of the synthesis, the sample was filtered, washed with acetone, and dried under ambient conditions. From the bulk material, which consisted of well-formed hexagonal prisms, a suitable single crystal was chosen for an X-ray study.[10] Since more than one amine was used in the synthesis, the product isolated contained some other contaminant phases. The other two phases typically seen in the synthesis are triclinic chabazite and anhydrous, condensed gallium phosphate. Since the experimental X-ray powder diffraction pattern of the bulk material is not monophasic (Figure 1a), we also calculated the powder pattern from the final atomic coordinates for reference (Figure 1b).

The asymmetric unit shown in Figure 2 is composed of two pentacoordinated galliums (Ga(1) and Ga(2); mean Ga−O 1.87 Å), one hexacoordinate gallium atom (Ga (3); mean Ga−O 1.93 Å) and three tetrahedral phosphorus atoms (mean P−O 1.54 Å, mean O−P−O 109.5°), linked to each of the gallium atoms via an oxygen bridge. The gallium coordination is completed by fluorine bridges (Ga(3)−F(1)−Ga(1), Ga(3)−F(2)−Ga(1); mean Ga−F 1.997 Å) between gallium atoms. Two of these asymmetric units are joined together through the six-coordinate gallium centers, through one fluorine and one oxygen bridge, resulting in a dimeric building unit, identical with that observed in ULM-8,[11] which in turn is bonded to six other identical moieties through Ga−O−P bonds.

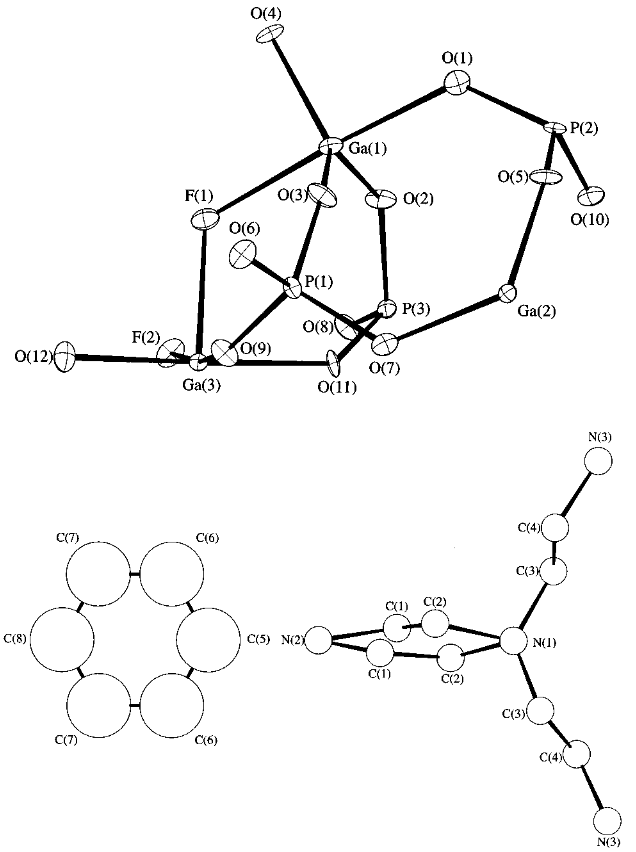

Figure 2. (a, top) Asymmetric unit of TREN−GaPO showing thermal ellipsoids (50% level). (b, bottom) The pyridine and TREN molecules shown with isotropic thermal spheres; note the disorder in the N(1)−C(2)−C(1)−N(2) chain.

Connecting the dimers in this manner generates a structure containing adjacent and parallel 12-ring and 8-ring channels in the [100] direction (Figure 3). The 12-ring has dimensions of 11.2 Å × 9.7 Å, as measured between oxygen centers. If van der Waals radii are assumed for the oxygens atoms, the approximate kinetic diameter of the ring would be 8.2 Å × 6.7 Å, slightly larger than faujasite. Perpendicular to these channels, down the [001] direction, is a 6-ring channel eclipsed by two fluorine atoms (Figure 4).

The TREN molecules have 2-fold orientation in the 12-ring channel whereas the pyridine molecules are stacked in a staggered fashion down the 8-ring channel, completely pore-filling the structure. The pyridine molecules reside in a region of the 8-ring channel that is open but bounded by the 8-rings (Figure 4). The segregation of the TREN into the larger channel and the pyridine into the smaller one is striking. The

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(10) Data were collected on an Enraf-Nonius CAD-4F diffractometer using monochromated Cu Kα radiation (full details are given in the supporting material) generated by a Rigaku rotating anode. The unit cell and orientation matrix were determined using automatic search and centering routines. Data were corrected for decay (15.78%), Lorentz, and polarization effects. The structure was solved by direct methods (SHELXS-86; Sheldrick, G., SHELXS-86 User Guide, Gottingen, Germany, 1986) and refined using least-squares analysis in the CRYSTALS suite of programs (Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS, University of Oxford, U.K., 1990). After refining the framework positions and anisotropic temperature factors, difference Fourier techniques were used to find the remaining non-hydrogen atoms. At this stage, the atoms within the pyridine and TREN molecules were unstable during the least squares refinement, so the carbon−carbon (TREN: C−C 1.54 Å; PYR: C=C 1.39 Å) and carbon−nitrogen (TREN: N−C 1.48 Å) distances and angles (TREN: central N 120.00°, C−C−N 108.00°; PYR C=C=C 120.00°) of both molecules were restrained to chemically sensible values with allowed ESDs of 0.01 Å. Isotropic temperature factors for each organic molecule were restrained to be equivalent since they each contain a large amount of disorder. After all of the atoms were found the following corrections were applied: DIFABS (Stewart, D.; Walker, N. *Acta Crystallogr. Sect. A* **1983**, *39*, 158), anomalous scattering, and finally a 2-term Chebychev weighting scheme. TREN-GaPO: $Ga_6P_6O_{24}F_4C_{12}N_4$, M_r = 1264.3, orthorhombic space group *Pnab*, a = 10.4057(3), b = 17.0231(3), c = 17.9919(3), Z = 4, D_c = 2.64 g cm^{-3}, $F(000)$ = 2396. Data were collected on a hexagonal crystal with dimensions of 0.12 × 0.18 × 0.05 mm. The total number of reflections measured was 11 139, of which 2600 were unique and 2332 had $I > 3\sigma(I)$. The refinement converged to give a final R = 0.075, R_w = 0.068.

(11) Serpaggi, F.; Loiseau, T.; Riou, D.; Ferey, G.; Hosseini, M. W. *Eur. J. Solid State Inorg. Chem.* **1994**, *31*, 595.

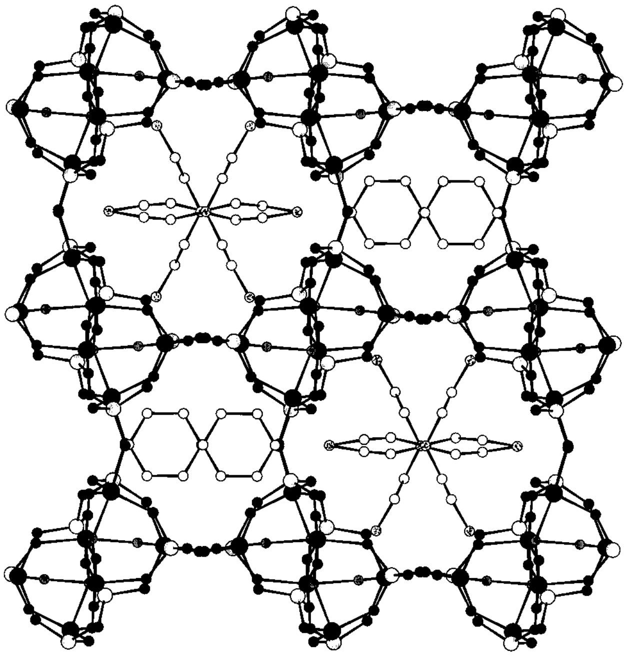

Figure 3. View of TREN−GaPO down the [100] direction. The TREN molecules are stacked in two orientations down the 12-ring channel and the pyridines are stacked in a staggered fashion down the 8-ring channel (large black circles, Ga; large shaded circles, P; small shaded circles, O/F; small open circles, C; small speckled circles, N).

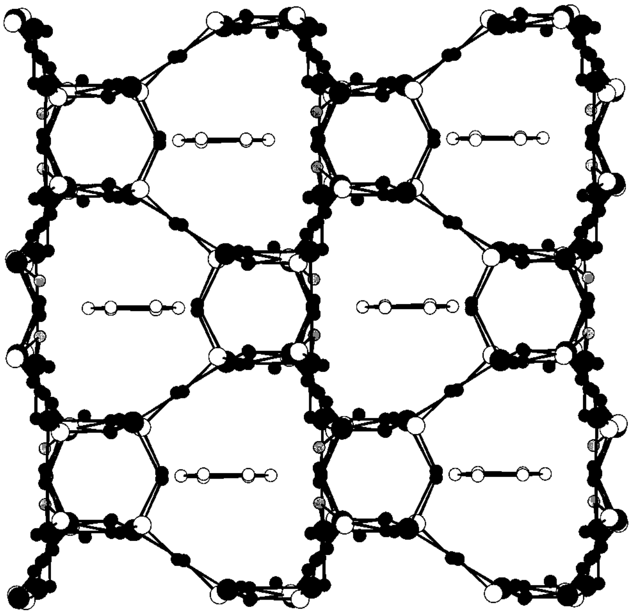

Figure 4. View down the [001] direction showing the eclipsed 6-rings and the stacking pattern of the pyridine molecules (atom types as in Figure 3).

hydrogen atoms were not located due to the disorder of the TREN molecules, so low-temperature studies are necessary to understand the hydrogen bonding in this structure. However, we assume that the four protons that are required for charge neutrality are located on the four nitrogens of the TREN molecule; TREN is a much stroger base, of course, than pyridine. Since the TREN seems to define the shape or "template" the 12-ring, we were curious to see if we could make a structure containing only 12-rings with TREN alone. When TREN is used exclusively in the synthesis, a layered material, ULM-8,[11] crystallizes. Protonated TREN molecules are found hydrogen bonded between the gallium oxyfluorophosphate layers. PYR−GaPO[12] and chabazite[13] form when only pyridine is used in the reaction. This clearly indicates that both amines are necessary for the formation of TREN−GaPO and that the amines are working cooperatively. Since the amines act conjointly, one probably as a structure directing agent and the other as a space-filling agent, the porosity could be controlled through the careful selection of the amine and solvent.

The DTA/TGA shows two distinct weight losses in oxygen, an endotherm at 380 °C and an exotherm at 500 °C, corresponding to the decomposition of the TREN and pyridine, respectively. This suggests that the TREN may be easily removed from the structure. Attempts to remove all of the organics using dry air or O_2 at 500 °C have resulted in the collapse of the structure on exposure to moist air. Low-temperature extraction techniques and limited exposure to water after calcination are currently underway so that the porosity of this material can be probed.

Since the gallium phosphate materials are quite sensitive to removal of the organic from the pore structure due to the strong interactions between the framework and the amine, we have tried to synthesize the aluminum version of TREN−GaPO. Crystallization of the $AlPO_4$ version of the structure is done in the same manner as the gallium phosphate. Aluminum sulfate, water, H_3PO_4, HF/pyridine, TREN, and pyridine were mixed together. The white gel was heated for 5 days at 170 °C. The resulting white powder contained TREN−$AlPO_4$, anhydrous $AlPO_4$ (berlinite) and a small amount of an unidentified phase. The lattice parameters of the TREN−$AlPO_4$ were found to be $a = 10.233(8)$ Å, $b = 16.67(1)$ Å, $c = 17.73(2)$ Å, which is consistent with the smaller size of Al^{3+} compared with Ga^{3+}. Further work is in progress to try to grow crystals of the TREN−$ALPO_4$ and to synthesize the SAPO version for catalytic testing.

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Supporting Information Available: Full details of the structure solution for TREN−GaPO, including tables of fractional atomic coordinates, selected interatomic distances, bond angles, anisotropic temperature factors (5 pages). Ordering information is given on any current masthead.

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